denominator approaches zero. Since all the other terms of the criterion remain finite, the diverging second derivative $d^2\xi/d\eta^2$ indicates that the Scott HEDCP cannot ever be a triple CP.

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(11) The extremal terms used here refer to figures as they are drawn. Their interpretation in terms of physical quantities can go either way: For instance, for the case of $\bar{\beta} > 0$, they also relate directly to the temperature; however, they have to be switched (a maximum for a minimum and vice versa) when discussed in terms of $\bar{g}$.
(12) Note that the system's trajectory, although linear in the actual interaction space, transforms in the compressed coordinates of Figure 4 into a hyperbolic curve diverging for $\varphi \to 0$ (i.e., $T \to 0$).

Polymer–Polymer Interaction Parameter in the Presence of a Solvent[1]

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ABSTRACT: A method is proposed to calculate the polymer–polymer interaction parameter (χ) from measurements performed on ternary systems composed of the polymer pair plus a solvent or probe. The usual methods of extracting χ from such measurements do not provide a true polymer–polymer interaction parameter because of the approximation of writing the residual chemical potential of the solvent in the ternary system as a sum of binaries. The equation-of-state theory gives a truly ternary chemical potential and can thus avoid such an approximation. The expressions needed to calculate the true polymer–polymer χ from such ternary theory are given. They are applied to obtain χ of the system PS + PVME from literature data determined by vapor sorption (VP) and inverse gas chromatography (IGC), with different solvents and probes. The results show that the method here proposed (a) gives χ from VP independent of the solvent used; (b) explains why the χ determined by IGC is probe dependent and predicts a correlation which allows for a probe-independent value of χ to be extracted, (c) shows that this probe-independent χ value from IGC is practically the same obtained from VP (by extrapolation to vanishing solvent concentration).

Introduction

In the last years, an important part of the applied polymer research has been aimed at preparing polymer blends to get new materials having improved properties and/or lower cost. The increasing interest in this field has led to the discovery of an ever-expanding number of compatible polymers. Miscibility in a polymer blend is controlled, as in any other mixture, by thermodynamic factors. Due to the extremely low values of the combinatorial entropy, a great many polymer pairs are incompatible, since a slightly positive mixing enthalpy is enough to prevent miscibility. Because of this, the majority of compatible polymer pairs are due to specific interactions such as hydrogen bonds.[2,3]

In the classical theory of Flory and Huggins,[4] the polymer–polymer interaction parameter χ_{ij} is used to describe the interaction between the two components of the blend. In general, the convention followed with regard to the values of this parameter is that high values are indicative of unfavorable interactions between the two components of the polymer blend, low values are indicative of slightly favorable interactions, and negative values appear when there are strong specific interactions between the two polymers.[3]

The polymer–polymer interaction parameter χ_{ij} can be determined by several techniques.[2,5,6] Among the most oftenly used ones are: inverse gas chromatography (IGC), vapor sorption (VP), osmometry, viscometry, and light scattering, melting point depression, small-angle X-ray scattering, and small-angle neutron scattering.

The techniques aforementioned can be divided in two groups, depending on the way χ_{ij} is obtained:

(1) Techniques that obtain χ_{ij} from measurements performed on the binary polymer–polymer system. Such are the melting point depression, whose usefulness is limited to the case in which one of the polymers in the mixture is crystalline and it gives χ_{ij} at a single temperature, the small-angle X-ray scattering and small-angle neutron scattering, whose usefulness is limited by the availability of the equipment and requires the deuteration of samples.

(2) Techniques more oftenly used, in which χ_{ij} is obtained from measurements performed on a ternary poly-

mer–polymer–solvent system. They correspond to the others mentioned. From them, osmometry, viscometry, and light scattering give χ_{ij} in a range of low concentration of the polymer blend in the solvent used; IGC on the contrary gives χ_{ij} at concentrations of the polymer blend close to one, and the technique of vapor sorption gives χ_{ij} in a broad range of intermediate concentrations.

In general, the values of χ_{ij} obtained for the same polymer blend by different techniques are not coincident.[5] Besides, the values of the polymer–polymer interaction parameter obtained from measurements performed in ternary systems depend significantly on the solvent used.[5,7,8] The discrepancies in the values of χ_{ij} are attributed to several factors, among them the pecularities of the techniques and differences inherent to the polymer samples studied, such as polydispersity, molecular weight, tacticity, crystallinity, etc.

In the present work we show that the way in which χ_{ij} is obtained in the case of ternary systems is only an approximation, which can lead to erroneous values of the polymer–polymer interaction parameter. The weakness of the approximation is to assume that the Gibbs mixing function for the ternary polymer–polymer–solvent system is additive with respect to the binary contributions. We propose here a method to avoid such approximation and show that then the values determined for the polymer–polymer interaction parameter result independent of the solvent used.

Theory

Definition of χ_{ij}. For a binary system polymer 2 + polymer 3, the Gibbs mixing function written according to the Flory–Huggins model is the sum of a combinatorial term plus an interaction term[9,10]

$$\Delta G_M/RT = n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_2\phi_3 g_{23} \qquad (1)$$

where n_i and ϕ_i are amount of substance and segment fraction of polymer i, respectively, and g_{23} is the interaction parameter describing the noncombinatorial part of ΔG_M. In eq 1, g_{23} is defined on the basis of segment fractions taking as reference volume the characteristic or reduction molar volume of component 2, V_2^*. If as reference volume the reduction molar volume of component 3, V_3^*, is taken, then ΔG_M reads:

$$\Delta G_M/RT = n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_3\phi_2 g_{32} \qquad (2)$$

By derivating eq 1 or 2 with respect to n_2, we obtain the chemical potential of component 2, $\Delta\mu_2/RT$, which is composed of a combinatorial term plus an interactional term usually called residual chemical potential, $\Delta\mu_2^R/RT$. The interaction parameter χ_{23} is then defined as the reduced residual chemical potential of component 2, $\Delta\mu_2^R/RT\phi_3^2$. It results as[11]

$$\chi_{23} = g_{23} + \phi_2\left[\frac{dg_{23}}{d\phi_2}\right] \qquad (3)$$

The derivation of eq 1 or 2 with respect to n_3 gives rise to the definition of a different interaction parameter, $\bar{\chi}_{23}$, as reduced residual chemical potential of component 3, $\Delta\mu_3^R/RT\phi_2^2$. It results as[11]

$$\bar{\chi}_{23} = g_{23} + \phi_3\left[\frac{dg_{23}}{d\phi_3}\right] \qquad (4)$$

Other interaction parameters can be defined, χ_{23}^v and $\bar{\chi}_{23}^v$, analogous to χ_{23} and $\bar{\chi}_{23}$, using eq 1 and 2 in terms of volume fractions instead of segment fractions.

Approximations. Determination of χ_{23} according to the preceding equations by direct measurements on the dry polymer blend is not always feasible, and χ_{23} is usually obtained from measurements of solvent activity in ternary mixtures polymer 2 + polymer 3 + solvent 1. The following relationship is then applied[12]

$$\chi_{1p} = \xi_2\chi_{12} + \xi_3\chi_{13} - \xi_2\xi_3\chi_{23}' \qquad (5)$$

where $\xi_i = \phi_i/(\phi_2 + \phi_3)$, $i = 2, 3$, ϕ_i being segment fraction in the ternary system. χ_{1p} is the interaction parameter determined in the ternary system; namely, $\chi_{1p} = \Delta\mu_1^R/RT\phi_p^2$, with $\phi_p = \phi_2 + \phi_3$. $\chi_{23}' = \chi_{23}V_1^*/V_2^*$.

Calculation of χ_{23} by means of eq 5 embodies two approximations. In the first approximation, the dependence of χ_{ij} on polymer concentration is neglected. This approximation can be avoided if the additivity is written in terms of the g_{ij} interaction parameters instead of in terms of the χ_{ij}'s. The correct relationship replacing eq 5 is then

$$g_{1p} = \xi_2 g_{12} + \xi_3 g_{13} - \xi_2\xi_3 g_{23}' \qquad (6)$$

In the case where the variation of g_{ij} with concentration were negligible, then eq 5 would be valid.

Because χ_{ij} tends to the value of g_{ij} when the polymer concentration approaches unity, the relationship eq 5 could be valid in the limit $\phi_1 \to 0$, which is practical in the experiments of IGC.

The second approximation consists of assuming that the interactional part of the Gibbs function for the ternary system is additive in the binary contributions. In the language of the Flory–Huggins model, it means that there is no ternary term depending simultaneously on ϕ_1, ϕ_2, and ϕ_3. The analysis of the thermodynamic properties of ternary systems polymer + two solvents in terms of equation-of-state theory has shown that the supposed additivity of binary interaction parameter terms is not good.[13,14] Therefore, g_{1p} cannot be taken as sum of binaries.

Ternary Theory. The Gibbs mixing function according to the more recent equation-of-state theories is composed of three contributions: combinatorial entropy, interactional exchange energy, and free volume. In the equation-of-state theory the noncombinatorial part of ΔG_M is not a sum of binary contributions. All terms depend simultaneously on the properties of the ternary system because the variable on which ΔG_M depends is the reduced temperature of the ternary 1 + 2 + 3 system (which is different from the reduced temperature of any of the binary systems).

Derivating the expression for the noncombinatorial part of ΔG_M for a ternary polymer 2 + polymer 3 + solvent 1 system, written according to Flory's equation-of-state theory, we get the residual chemical potential of the solvent as[15]

$$\frac{\Delta\mu_1^R}{RT\phi_p^2} = \chi_{1p} = \frac{p_1^*V_1^*}{RT\phi_p^2}\left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}} - 3\tilde{T}_1 \ln \frac{\tilde{V}^{1/3} - 1}{\tilde{V}_1^{1/3} - 1}\right] + \frac{V_1^*}{RT\phi_p^2\tilde{V}}\left[X_{12}\theta_2(1 - \theta_1) + X_{13}\theta_3(1 - \theta_1) - \theta_2\theta_3\frac{s_1}{s_2}X_{23}\right] \qquad (7)$$

where p_i^*, V_i^*, T_i^*, are the characteristic or reduction parameters of the pure components for pressure, molar volume, and temperature, respectively, and the tilde denotes reduced quantities. $\tilde{V}$ is the reduced volume of the ternary system. X_{ij} is the exchange interaction energy density (also called interaction parameter in the theory). θ_i and ϕ_i are molecular surface fractions and segment fractions, respectively. s_i is molecular surface to volume ratio (or number of contact sites per segment).

It can be seen in eq 7 that the interaction parameter χ_{1p} contains a balance of exchange interaction energy terms, which apparently is additive in the binary contributions (the square bracket enclosing X_{ij}'s). However, this square bracket is multiplied by a ternary quantity ($\tilde{V}$), which destroys additivity. Each term is really of the form $X_{ij}/\tilde{V}$, thus ternary because of its dependence on the third component besides i and j. χ_{1p} contains also another contribution (the first square bracket in eq 7), which reflects primarily free volume. This is also ternary (depends on $\tilde{V}$) and has no counterpart in the Flory–Huggins model (eq 5).

In order to write the χ_{1p} parameter in terms of the corresponding binary parameters χ_{ij}, so as to obtain an expression equivalent to the Flory–Huggins eq 5, we substitute the X_{ij} terms in eq 7 by their corresponding χ_{ij}'s written according to equation-of-state theory for the binary i–j system, which is[16]

$$\chi_{ij} = \frac{V_i^*}{\tilde{V}_{ij}}\frac{X_{ij}}{RT}\frac{\theta_j^2}{\phi_j^2} + \frac{p_i^* V_i^*}{RT\phi_j^2}\left[\frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}_{ij}} - 3\tilde{T}_i \ln \frac{\tilde{V}_{ij}^{1/3} - 1}{\tilde{V}_i^{1/3} - 1}\right] \tag{8}$$

with $\tilde{V}_{ij}$ the reduced volume of the binary i–j system.

In order to perform such a substitution, it is necessary to choose properly the concentrations of the corresponding binary systems. For χ_{1j} ($j = 2, 3$), we take ϕ_j in eq 8 as $\phi_j = \phi_2 + \phi_3 = \phi_p$; and for χ_{ij} ($i = 2$, $j = 3$), we take $\phi_j = \phi_3/\phi_p = \xi_j$, where ϕ_1, ϕ_2, and ϕ_3 are segment fractions in the ternary system. Such a choice is tantamount to assuming that the solvent in the ternary system is distributed among the two binary polymer–solvent systems in proportion to the fraction of each polymer in the blend.

Accordingly

$$\chi_{1p} = \chi_{12}\frac{\tilde{V}_{12}}{\tilde{V}}\frac{\theta_2\theta_p}{\theta_{2B}^2} + \chi_{13}\frac{\tilde{V}_{13}}{\tilde{V}}\frac{\theta_3\theta_p}{\theta_{3B}^2} - \chi_{23}'\frac{\tilde{V}_{23}}{\tilde{V}}\frac{\phi_2\phi_3}{\phi_p^2}\frac{\theta_p^2}{\phi_p^2}\frac{s_1}{s_3} + \Gamma \tag{9}$$

where Γ is a free volume term given by

$$\Gamma = \frac{p_1^* V_1^*}{RT\phi_p^2}\left[\Gamma_{1p} - \frac{\tilde{V}_{12}}{\tilde{V}}\frac{\theta_2\theta_p}{\theta_{2B}^2}\Gamma_{12} - \frac{\tilde{V}_{13}}{\tilde{V}}\frac{\theta_3\theta_p}{\theta_{3B}^2}\Gamma_{13}\right] + \frac{p_2^* V_1^*}{RT\phi_p^2}\frac{\tilde{V}_{23}}{\tilde{V}}\frac{s_1}{s_2}\frac{\theta_2}{\theta_3}\theta_p^2\Gamma_{23} \tag{10}$$

where $\Gamma_{ij} = \tilde{V}_i^{-1} - \tilde{V}_{ij}^{-1} - 3\tilde{T}_i \ln (\tilde{V}_{ij}^{1/3} - 1)/(\tilde{V}_i^{1/3} - 1)$ and $\theta_{iB} = s_i\phi_p/(s_1\phi_1 + s_i\phi_p)$, with $i = 2, 3$. θ_p is $\theta_p = \theta_2 + \theta_3$.

Equation 9 gives χ_{1p} as a sum of three terms, each containing a different binary interaction parameter, plus the Γ term. This additive combination of binary interaction parameters comes naturally from the Gibbs mixing function, when written according to equation-of-state theory, and has nothing to do with any a priori assumption about the additivity of binary terms in ΔG_M.

Equation 9 is of general validity and contains no simplification (other than the equation-of-state theory itself). It can be applied to any polymer–polymer–solvent system, at any total polymer concentration, ϕ_p, and any blend composition, ξ.

In order to calculate χ_{23} from eq 9, the full information allowing the calculation of reduced volumes for the ternary system, $\tilde{V}$, and for the corresponding binaries, $\tilde{V}_{ij}$, as well as the components surface-to-volume ratios, s_i, are needed.

Equation 9 differs from eq 5 in two important ways. First, the binary interaction parameters enter multiplied by surface fractions instead of segment fractions. Second, there is the free volume contribution represented by the Γ (also the $\tilde{V}_{ij}/\tilde{V}$ factors). Surface fractions have been used before to obtain an expression for χ_{23}[17] but using the Flory–Huggins theory (thus additive) and in the limit of vanishing solvent ($\phi_p \rightarrow 1$) only.

Simplified Cases. In each polymer–polymer–solvent system, the discrepancy between the χ_{23} calculated according to our eq 9 and the χ_{23} calculated according to eq 5 would be different. However, in order to get a feeling on the possible importance of these discrepancies, we consider now two cases: (a) an extreme simplification of eq 9; (b) the limit of eq 9 for vanishing solvent concentration ($\phi_p \rightarrow 1$).

Let us call χ_{23}^T the value of χ_{23} that is obtained from χ_{23}' calculated by means of the ternary theory eq 9, and χ_{23}^A the value of χ_{23} that is obtained from the additivity approximation eq 5.

Case a. We simplify eq 9 as much as possible by introducing the following simplifications:

(1) The reduced volumes of the two polymers and of their blends are approximately equal: $\tilde{V}_2 = \tilde{V}_3 = \tilde{V}_{23}$.

(2) The reduced volumes of the mixtures containing solvent are approximately equal: $\tilde{V}_{12} = \tilde{V}_{13} = \tilde{V}_{1p}$.

(3) $s_2 = s_3$.

For a number of polymer pairs $\tilde{V}_2 \simeq \tilde{V}_3$ and also $\tilde{V}_2 \simeq \tilde{V}_{23}$ (unless X_{23} is large). Therefore, simplification (1) can be good in certain cases. Simplification (2) is usually less acceptable and simplification (3) is clearly rough.

By equating eq 9 and 5, we obtain in this case a:

$$\chi_{23}^A = \chi_{23}^T\frac{\tilde{V}_3}{\tilde{V}}\frac{s_1}{s_3}\frac{\theta_p^2}{\phi_p^2} \tag{11}$$

The same result would have been obtained if $\chi_{12} = \chi_{13} = 0$. Equation 11 shows that the difference between χ_{23}^A and χ_{23}^T is dependent on the solvent and on the polymer concentration. For this reason, the error that is committed when the interaction parameter is identified with χ_{23}^A will depend on the technique used for its determination and on the solvent. Such a difference lies in between the limits

$$\left(\frac{\chi_{23}^A}{\chi_{23}^T}\right)_{\phi_p=1} = \frac{s_1}{s_3} \qquad \left(\frac{\chi_{23}^A}{\chi_{23}^T}\right)_{\phi_p=0} = \frac{s_3}{s_1}\frac{\tilde{V}_3}{\tilde{V}_1}$$

Common values of s_1/s_3 are around 2 and common values of $\tilde{V}_1/\tilde{V}_3$ are around 1.2. Therefore, polymer–polymer interaction parameters calculated via the usual additivity approximation can be anywhere between about twice an about half of the true value of the interation parameter (in this very simplified case a).

Case b. Limit of $\phi_p \rightarrow 1$. In this case we consider the limit of eq 9 for $\phi_p \rightarrow 1$, without introducing any approximation. The polymer concentration chosen in this case ($\phi_p \rightarrow 1$) corresponds to the experimental conditions met in IGC. In this limit, we obtain

$$\chi_{23}^A = \chi_{23}^T\frac{s_1}{s_3} + (\chi_{12} - \chi_{13})\frac{(s_3 - s_2)V_2^*}{(\phi_2 s_2 + \phi_3 s_3)V_1^*} - \kappa \tag{12}$$

with κ a term containing Γ.[18]

This eq 12 is of general validity for $\phi_p \rightarrow 1$ and contains no approximation. It can be easily simplified by assuming $\tilde{V}_2 = \tilde{V}_3 = \tilde{V}_{23}$ (simplification (1) above). Of the three simplifications used before, this is the lest stringent one. In the present limit of $\phi_p \rightarrow 1$, simplification (1) is enough to render $\kappa = 0$.

Equation 12 gives an answer to why the interaction parameters determined by IGC are dependent on the

Table I
Equation-of-State Parameters, at 25 °C

pure component[a]	p^*, J·cm^{-3}	T^*, K	v_{sp},* cm^3·g^{-1}	v_{sp},[b] cm^3·g^{-1}
Cl_3CH	636	4450	0.5124	0.6759
C_6H_6	628	4709	0.8860	1.1444
PS	547	7420	0.8100	0.9336
PVME	546	7201	0.8284	0.9551

[a] Reference 20. [b] Specific volume.

probe: they depend on the difference in solvent quality of the probe with regard to the two polymers in the blend, $\chi_{12} - \chi_{13}$, and on the number of contact sites per segment of the solvent, s_1.

If it also holds that $\chi_{12} = \chi_{13}$ or $s_2 = s_3$, then:

$$\chi_{23}{}^{A} = \chi_{23}{}^{T}\frac{s_1}{s_3} \tag{13}$$

Again, the additivity approximation gives values that can be around twice the value of the true polymer–polymer interaction parameter.

The simplifications introduced into the general eq 9 and 12 cause the free-volume terms Γ and κ to vanish. The main factor that remains then is the difference in surface-to-volume ratios. But, for a general application of eq 9 and 12, the free-volume differences should be properly taken into account through calculation of the actual values of Γ and κ.

Calculations

The system chosen for a first test of the validity of eq 9 has been the blend polystyrene (PS) + poly(vinyl methyl ether) (PVME), since this is one of the systems most extensively studied in the literature and for which there are values of χ_{23} obtained through the additivity approximation (eq 5) in a broad range of polymer concentrations and also values of χ_{23} obtained through techniques that do not require the presence of a solvent.

We now discuss the values of χ_{23} calculated through eq 9 compared with those obtained from different techniques through the additivity approximation.

(A) Vapor Pressure. The values of χ_{23} have been obtained as a function of ϕ_p with the technique of vapor pressure by Panayiotou and Vera for two solvents:[19,20] PS(2) + PVME(3) + Cl_3CH(1), $0.6 < \phi_p < 0.9$ and ξ_2 = 0.329, 0.597, 0.798; PS(2) + PVME(3) + C_6H_6(1) $0.4 < \phi_p < 0.9$ and ξ_2 = 0.329, 0.798. The molecular weights of the samples are $M_{PS} = 800$ and $M_{PVME} = 14000$. The quantities needed for the application of eq 9 have been taken from ref 20 and are given in Table I. The values of s_3 and s_2 have been estimated using a cylinder model for the polymer units, with the results $s_3 = 0.64 \times 10^8$ cm^{-1} and $s_2 = 0.48 \times 10^8$ cm^{-1}.

In these particular two systems, $\tilde{V}_2 \simeq \tilde{V}_3 \simeq \tilde{V}_{23}$. For example, for the blend composition $\xi_2 = 0.5969$ (solvent Cl_3CH; different values of total polymer concentration, ϕ_p), we have: $\tilde{V}_{23} = 1.155$, and $\tilde{V}_2$ and $\tilde{V}_3$ are both equal to 1.153. Also, $\tilde{V}_{12} \simeq \tilde{V}_{13} \simeq \tilde{V}$. For example, for the same blend composition and total polymer concentrations ϕ_p = 0.7443, 0.8202, and 0.8612, we have $\tilde{V}_{12}$ = 1.192, 1.180, and 1.174, $\tilde{V}_{13}$ = 1.190, 1.181, and 1.175, and $\tilde{V}$ = 1.191, 1.180, and 1.174, respectively. Because of this similarity in reduced volumes, the influence of function Γ of eq 9 in these systems is small. As an illustration, we give the values calculated for Γ at the same blend composition and total polymer concentrations (in the same order as above): $\Gamma = -3 \times 10^{-3}$; 4×10^{-5}; 2×10^{-3}. These values of Γ are small compared with the terms containing χ_{1p}, χ_{12}, and χ_{13} in eq 9, and the influence of Γ on the value of χ_{23} is of the order of 10% or less. For this reason and trying to simplify the calculation, we have taken for both systems Γ = 0. These systems provide thus only a partial test of eq 9. Other systems, having larger influence of Γ, should be considered for a fuller test of eq 9.

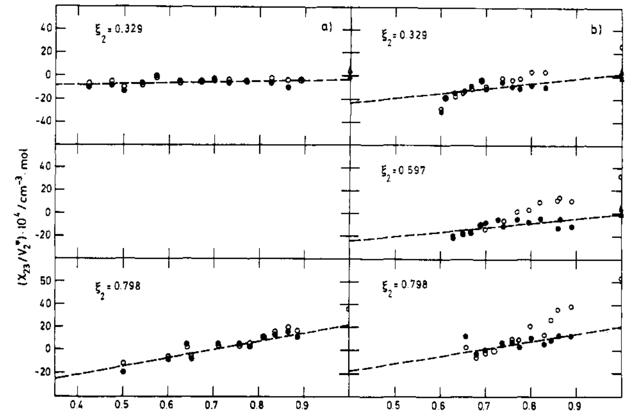

Figure 1. Polymer–polymer interaction parameter, χ_{23}/V_2^*, vs polymer concentration, ϕ_p, for the systems (a) PS(2) + PVME(3) + C_6H_6(1) and (b) PS(2) + PVME(3) + Cl_3CH(1), at 25 °C. Experimental results from vapor sorption measurements reported in ref 19. (○) Values of $\chi_{23}{}^{A}$ from ref 19. (●) Values of $\chi_{23}{}^{T}$ obtained in this work. (△) Obtained from inverse gas chromatography results as explained in the text.

Table II
Values of Polymer–Polymer Interaction Parameter, χ_{23}/V_2^*, at $\phi_p \rightarrow 1$, from Vapor Sorption Measurements, for the System PS(2) + PVME(3), at 25 °C

syst	ξ_2	$(\chi_{23}/V_2^*)_{\phi\rightarrow 1}$, $\times 10^4$ mol·cm^{-3}	
		χ^A (eq 5)	χ^T (eq 9)
PS(2) + PVME(3) + C_6H_6	0.329	-4	-3
	0.798	36	27
PS(2) + PVME(3) + Cl_3CH	0.329	26	-1
	0.597	33	2
	0.798	63	23

The values of χ_{12} and χ_{13} vs ϕ_p have been taken also from ref 19.

The results obtained in our calculation of the polymer–polymer interaction parameter are shown in Figure 1. We have plotted the interaction parameter as χ_{23}/V_2^* in order to have values that are not dependent on the solvent used in the measurements and can thus be compared more properly in the two systems.

We can see that there is a difference in the values of χ_{23}/V_2^* obtained by us and those obtained through the additivity approximation. Such a difference becomes more noticeable in the case of the system PS(2) + PVME(+) + Cl_3CH(1), and in both systems the difference is larger with higher value of ϕ_p, within the range of concentrations measured.

It is of note that, for a given composition of the blend, the values of χ_{23}/V_2^* obtained through the additivity approximation are solvent-dependent; that is, in the range of ϕ_p covered, there is a discrepancy in the dependence of χ_{23}/V_2^* with ϕ_p between the system with benzene and the system with chloroform. However, the values obtained through eq 9 do not show such a discrepancy, and the dependence of χ_{23}/V_2^* with ϕ_p, for a given composition of the blend, is similar in both systems studied.

This can be better appreciated in Table II, where we compare the values of χ_{23}/V_2^* extrapolated to $\phi_p \rightarrow 1$ from the χ_{23}/V_2^*'s calculated according to eq 5 and according

Table III
Polymer–Polymer Interaction Parameter, χ_{23}/V_2^*, from Inverse Gas Chromatography Measurements, for the System PS(2) + PVME(3), at 40 °C

probe	$\Delta\chi$	χ_{23}^A/V_2^*, $\times 10^4$ mol·cm^{-3} ϕ_2 = 0.444	χ_{23}^A/V_2^*, $\times 10^4$ mol·cm^{-3} ϕ_2 = 0.619	s_1, $\times 10^8$ cm^{-1}
n-hexane	−0.19	0.0	−8.6	1.41
n-heptane	−0.20	1.5	−6.9	1.40
n-octane	−0.19	−2.1		1.42
2,2,4,4-tetramethylpentane	−0.42	−0.7	−8.8	1.41
cyclopentane	−0.50	9.6	−2.4	1.32
cyclohexane	−0.52	1.2	−11.8	1.32
benzene	0.11	15.2	7.6	1.16
toluene	0.05	11.7	7.4	1.25
isopropyl ether	0.02	2.4	6.4	1.42
p-dioxane	0.23	14.5	0.0	1.64
propyl acetate	0.27	5.9	−3.9	1.43
acetone	0.33	4.3	38.3	1.50
2-butanone	0.34	22.6	3.5	1.46
carbon tetrachloride	0.23	17.4	1.2	1.45
dichloromethane	0.73	52.5	24.5	1.25
tetrachloroethene	0.02	10.7	2.15	1.35
trichloroethene	0.45	29.3	7.3	1.39
fluorobenzene	0.37	21.6	8.4	1.25

to eq 9.

From the results on Table II we can see the following:

(a) The values of χ_{23}/V_2^* obtained in this work are notably lower (reaching even change of sign) than those obtained with the additivity approximation. Our results are much closer to the interaction parameter values reported for the dry blend by small-angle neutron scattering measurements.[21-23]

(b) The values of χ_{23}/V_2^* for a given composition of the blend are independent of the solvent used, which seems to indicate that the method described in this work for the calculation of χ_{23} serves adequately to take out the effect of the solvent, contrary to the method of calculation based in eq 5.

(c) The dependence of χ_{23}/V_2^* on the composition of the blend, ξ_i, is entirely analogous in the two systems studied. (In both cases a tendency toward a greater compatibility is observed as the system becomes increasingly rich in PVME. This is contrary to the SANS results where an increasingly lower χ_{23} is found as the proportion of PS increases.[23] However, the SANS results refer to deuterated PS and to different temperatures.)

(B) Gas Chromatography. With the purpose of testing eq 12 and of comparing the interaction parameters determined by IGC using and avoiding the additivity approximation, we have used the data of Su and Patterson,[24] who have determined the interaction parameter $\chi_{23}'^A$ by IGC, for blends of PS(2) + PVME(3) (molecular weights M_{PS} = 600, M_{PVME} = 10 000) of segment fraction composition ϕ_2 = 0.444 and ϕ_2 = 0.619, at 40 °C, using 20 different solvents as probes.

In Table III are shown the values χ_{23}^A/V_2^* that are obtained from the experimental ones of $\chi_{23}'^A$ given by these authors. It is better to deal with χ/V_2^* than with χ', because χ' is defined taking the molecular size of the solvent as reference, $\chi_{23}' = \chi_{23}V_1^*/V_2^*$, and dividing through V_1^* eliminates this solvent size dependence. We can see in Table III that the resulting χ_{23}^A/V_2^* values are still dependent on the solvent and cannot be taken as real interaction parameters reflecting just the polymer–polymer interactions.

In fact, the χ_{23}^A/V_2^* values are correlated with $\chi_{12} - \chi_{13}$, the value of χ_{23}^A/V_2^* being high with larger $\Delta\chi$. This correlation is predicted by our eq 12. In order to compare with the experimental results of Table III, we rewrite this eq 12 in the following form (neglecting for the moment κ because of the applicablility of simplification (1) in this particulr polymer blend):

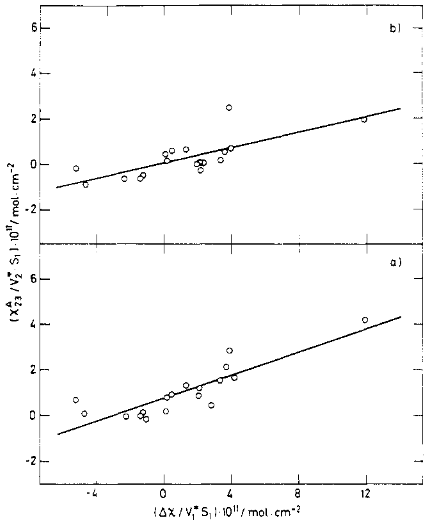

Figure 2. Polymer–polymer interaction parameter, $\chi_{23}/V_2^*s_1$, vs $\Delta\chi/V_1^*s_1$ ($\Delta\chi \equiv \chi_{12} - \chi_{13}$), for the system PS(2) + PVME(3) + probe(1), at 40 °C. (a) ϕ_2 = 0.444; (b) ϕ_2 = 0.619. Experimental results from inverse gas chromatography measurements reported in ref 24.

$$\frac{\chi_{23}^A}{V_2^*s_1} = \frac{\chi_{23}^T}{V_2^*s_3} + \frac{(\chi_{12} - \chi_{13})}{V_1^*s_1}\,\frac{(s_3 - s_2)}{(\phi_2 s_2 + \phi_3 s_3)} \tag{14}$$

The plot of $\chi_{23}^A/V_2^*s_1$ versus $\Delta\chi/V_1^*s_1$ should be linear with slope $(s_3 - s_2)/(\phi_2 s_2 + \phi_3 s_3)$ and intercept $\chi_{23}^T/V_2^*s_3$. Such a type of plot is shown in parts a and b of Figure 2 for the blends of ϕ_2 = 0.444 and ϕ_2 = 0.619, respectively. The values of s_1 needed have been calculated according to Bondi;[25] they are shown on Table III. As we can see in parts a and b of Figure 2, a good linear correlation is obtained, which confirms the adequacy of eq 12. Even more, the slopes of these straight lines are 0.26 (for ϕ_2 = 0.444) and 0.20 (for ϕ_2 = 0.619), and the respective theoretical values calculated from eq 14 (taking $s_3 = 0.64 \times 10^8$ cm^{-1} and $s_2 = 0.48 \times 10^8$ cm^{-1} estimated as explained above) are 0.286 and 0.296, respectively, showing thus a good accord.

The error that we have commited by neglecting κ is very small. With the data of $\tilde{V}_1$, $\tilde{V}_2$, $\tilde{V}_3$, and $\tilde{V}_{23}$, we have calculated κ for several probes. The results show that κ represents 5% or less of the value obtained for χ_{23}^T.

We can compare the solvent-independent interaction parameter deduced now from IGC measurements (through eq 12), with the one obtained above from vapor pressure measurements (through eq 9), for the same total polymer concentration $\phi_p \rightarrow 1$. From the intercepts of Figure 2 we calculate the interaction parameter values from IGC as $\chi_{23}^T/V_2^* = 4.9 \times 10^{-4}$ and 0.5×10^{-4}, for ϕ_2 = 0.444 and 0.619, respectively. These two values obtained from IGC are shown in Figure 1. We can see that the agreement with the values of vapor pressure calculated through our eq 9 and extrapolated to $\phi_p \rightarrow 1$ is excellent (for similar blend compositions).

We can conclude, then, that the solvent dependence of χ_{23}^A obtained by IGC is basically due to the additivity approximation and that only in those experiments in which $\Delta\chi = 0$ or in which $\Delta\chi$ maintains an approximately constant value (for all the solvents probed) can the values of χ_{23}^A be approximately independent of solvent (except for its variation with s_1).

Macromolecules **1989,** *22,* 4351-4361

Conclusion

The perturbing influence of solvent (or probe) on the value of the polymer–polymer interaction parameter (χ), and the differences in χ values obtained by means of different experimental techniques, can be effectively minimized using the method of calculation of χ here proposed, which is based on equation-of-state *ternary* theory. This conclusion holds for the typical polymer pair here studied but should be extended to other systems (especially those having larger free-volume differences).

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Registry No. PS, 9003-53-6; PVME, 9003-09-2; C_6H_6, 71-43-2; Cl_3CH, 67-66-3; hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; 2,2,4,4-tetramethylpentane, 1070-87-7; cyclopentane, 287-92-3; cyclohexane, 110-82-7; toluene, 108-88-3; isopropyl ether, 108-20-3; *p*-dioxane, 123-91-1; propyl acetate, 109-60-4; acetone, 67-64-1; 2-butanone, 78-93-3; carbon tetrachloride, 56-23-5; dichloromethane, 75-09-2; tetrachloroethene, 127-18-4; trichloroethene, 79-01-6; fluorobenzene, 462-06-6.

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(18) $\kappa = (V_2^*/V_1^*)\{\Gamma/\xi_2\xi_3 + \chi_{12}(\tilde{V}_2/\tilde{V}_{23} - 1)[\xi_3^{-1} + (s_2 - s_3)/(\xi_2 s_2 + \xi_3 s_3)] + \chi_{13}(\tilde{V}_3/\tilde{V}_{23} - 1)[\xi_2^{-1} - (s_2 - s_3)/(\xi_2 s_2 + \xi_3 s_3)]\}$ with Γ of eq 10 taken at $\phi_p \rightarrow 1$.
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Melting and Crystallization Kinetics of a High Molecular Weight *n*-Alkane: $C_{192}H_{386}$

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ABSTRACT: The fusion process and the crystallization kinetics from the pure melt of the *n*-alkane $C_{192}H_{386}$ have been studied. Several fundamental features of these processes have emerged. At room temperature the compound is completely crystalline, consistent with the formation of molecular crystals, while premelting is observed at elevated temperatures. A theoretical basis is presented for the premelting. The possibility of premelting in the other *n*-alkanes suggests the need to reexamine the analysis of the melting temperature–composition relations for such species. The crystallization kinetics from the pure melt obey classical theory. The temperature coefficient of the crystallization process indicates that it is nucleation controlled and follows the theory developed for chains of finite molecular weight. Analysis of this kinetic data allows for a connection to be made between the crystallization of low and high molecular weight chains.

Introduction

The recent synthesis of very high molecular weight *n*-alkanes[1-3] has provided a set of model compounds whose study will allow for a further understanding of the fusion–crystallization process in general and that of polymers in particular. Studies with these compounds can serve as a bridge to the crystallization behavior of polymers by comparing the characteristics of these *n*-alkanes with low molecular weight linear polyethylene fractions crystallized from either the bulk or from dilute solution.[4-8] Comparable molecular weights from both classes of compounds are now available. The very close connection between the

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